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(21) International Application Number: PCT/US00/11746 (22) International Filing Date: 1 May 2000 (01.05.00) (30) Priority Data: 60/132,453 4 May 1999 (04.05.99) US (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): PETROV, Viacheslav, Alexandrovich [US/US]; 2 Cappa Court, Hockessin, DE 19707 (US). FEIRING, Andrew, Edward [US/US]; 7 Buck- ridge Drive, Wilmington, DE 19807 (US). FELDMAN, Jer- ald [US/US]; Brackenville Woods, 16 Cinnamon Drive, Hockessin, DE 19707 (US). (74) Agent: MAGEE, Thomas, H.; E.I. Du Pont De Nemours And Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: POLYFLUORINATED EPOXIDES AND ASSOCIATED POLYMERS AND PROCESSES (57) Abstract A method for producing partially fluorinated epoxides and corresponding polyether homopolymers of these polyfluorinated epoxides is described. Also described is a method for incorporating a fluoroalcohol functional group into a polymer as a pendant group. Certain perfluorinated olefins are also described. These polyfluorinated epoxides and the associated polymers and methods relating to them are useful components in photoresists, particularly in lithographic photoresists for use at low ultraviolet wavelengths (e.g., 157 nm).		

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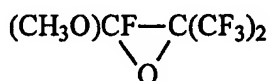
TITLE
POLYFLUORINATED EPOXIDES AND
ASSOCIATED POLYMERS AND PROCESSES
BACKGROUND OF THE INVENTION

5 1. Field of the Invention

This invention is in the field of polyfluorinated epoxides and includes methods for producing these epoxides, certain chemical reactions these epoxides undergo, and monomers and polymers derived from these epoxides and/or their derivatives.

10 2. Description of Related Art

Various polyfluorinated epoxides are known. As an illustrative example, 1,1-bis(trifluoromethyl)ethylene oxide is known and can be produced by reaction of diazomethane and hexafluoroacetone: see Chang, I. S., Willis, C. J., Can. J. Chem. 1997, 55, 2465. While this production method can be done on a lab scale, 15 it does involve use of hazardous diazomethane and is not capable of being scaled up for producing larger quantities. As a second illustrative example, the compound illustrated below is also known.



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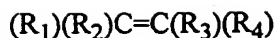
The production of this compound, again involving a hazardous reagent, has been reported via oxidation of the corresponding olefin with ozone. See JP Patent Publication 08333302 A2. Neither of the aforementioned production processes is attractive for commercial production for the reasons presented above.

25 The preparation of perfluorinated or perhalogenated epoxides using sodium hypochlorite or sodium hypobromide is known. See: Kolenko, I. P., Filaykova, T. I., Zapevalov, A. Yu., Lur'e, E. P. Izv. AN USSR. Ser. Khim. 1979, p. 2509; and Coe, P. L., Mott, A. W., Tatlow, J. C., J. Fluorine Chemistry, 1985, V30, p. 297.

30 There is a need for a safe and efficient production method for producing polyfluorinated epoxide compounds as well as safe efficient processes for converting them into useful polymeric products.

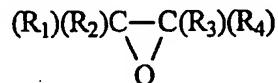
SUMMARY OF THE INVENTION

35 In one embodiment, the invention is a method for producing a fluorinated epoxide in high yield, said method comprising the step of reacting a fluorinated ethylenically unsaturated compound having the structure:



with a metal hypohalite oxidizing agent in the presence of a phase transfer catalyst to produce the fluorinated epoxide having the structure:

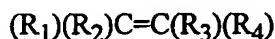
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wherein R_1 is selected from the group consisting of H and OR, where R is C_1 - C_{10} alkyl; R_2 is selected from the group consisting of H and F; and R_3 and R_4 are
10 selected from the group consisting of C_1 - C_{10} perfluoroalkyl and C_1 - C_{10} perfluoroalkoxy.

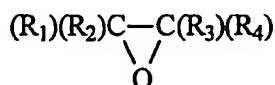
In another embodiment, the invention is a method for producing a fluorinated epoxide in high yield, said method comprising the step of reacting a fluorinated ethylenically unsaturated compound having the structure:

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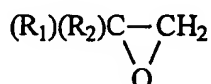
with a metal hypohalite oxidizing agent in the presence of a phase transfer catalyst to produce the fluorinated epoxide having the structure:

20



wherein R_1 is selected from the group consisting of H and OR, where R is C_1 - C_{10} alkyl; R_2 is selected from the group consisting of H, F, C_1 - C_{10} perfluoroalkyl, and
25 X-substituted C_1 - C_{10} alkyl, wherein X is F, Cl, Br, I, OH, or OR; R_3 and R_4 are each independently selected from the group consisting of C_1 - C_{10} perfluoroalkyl, $C(R_f)(R_f')OH$ where R_f and R_f' are C_1 - C_{10} perfluoroalkyl groups, C_1 - C_{10} perfluoroalkoxy, C_1 - C_{10} carboalkoxy, and hydroxy-substituted C_1 - C_{10} carboalkoxymethyl-substituted C_1 - C_4 perfluoroalkyl.

30 In another embodiment, the invention is a method for producing a polyfluorinated polyether in high yield, said method comprising the step of reacting a fluorinated epoxide having the structure:



with a basic compound in solution to produce the polyfluorinated polyether having the repeat unit:



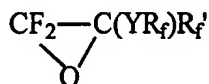
wherein R_1 and R_2 are independently C_1 - C_{10} perfluoroalkyl.

In another embodiment, the invention is a fluorine-containing polymer comprising a repeat unit derived from at least one ethylenically unsaturated
10 compound containing a fluoroalcohol functional group having the structure:



wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to about
15 10 carbon atoms or taken together are $(CF_2)_n$ wherein n is 2 to 10; and X is selected from the group consisting of sulfur, oxygen, nitrogen, phosphorous, other Group Va element, and other Group VIa element.

In yet another embodiment, the invention is a perfluorinated epoxide having the structure:
20



where R_f and R_f' are the same or different perfluoroalkyl groups of from 1 to about 10 carbon atoms or taken together are $(CF_2)_n$ wherein n is 2 to 10; and Y is
25 selected from the group consisting of sulfur and oxygen.

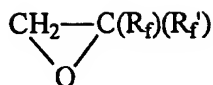
In still another embodiment, the invention is a method for incorporating a fluoroalcohol functional group having the structure:



into a polymer as a pendant group, wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms or taken together are $(CF_2)_n$ wherein n is 2 to 10; and X is selected from the group consisting of sulfur, oxygen, nitrogen, phosphorous, other Group Va element, and other Group VIa
35 element;

said method comprising the steps of:

a. reacting an epoxide having the structure:



5 with an ethylenically unsaturated compound containing
substituent X to produce an ethylenically unsaturated comonomer
comprised of the structure:



and

- 10 b. polymerizing a reaction mixture comprised of the ethylenically
unsaturated comonomer to produce the polymer.

In still another embodiment, the invention is a compound of structure



15 where R_a is an ethylenically unsaturated alkyl group of from 2 to 20 carbon
atoms, optionally substituted by one or more ether oxygens and R_f and R_f' are the
same or different perfluoroalkyl groups of from 1 to about 10 carbon atoms or
taken together are $(\text{CF}_2)_n$ wherein n is 2 to 10, and X is selected from the group
20 consisting of sulfur, oxygen, nitrogen, phosphorous, other Group Va element, and
other Group VIa element.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

In one embodiment, the invention is a method for producing a fluorinated
epoxide comprising the step of reacting a fluorinated ethylenically unsaturated
25 compound (structure given supra) with a metal hypohalite oxidizing agent in the
presence of a phase transfer catalyst to produce the fluorinated epoxide (structure
also given supra).

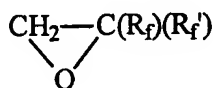
A suitable oxidizing agent is a metal hypohalite. Exemplary metal
hypohalites include, but are not limited to, various metal hypochlorites or metal
30 hypobromites, including lithium, sodium, potassium, and calcium hypochlorites or
hypobromites. Preferred oxidizing agents are sodium, calcium, or potassium
hypochlorite and sodium or potassium hypobromite.

Examples of suitable phase-transfer catalysts include, but are not limited
to, tetraethylammonium chloride, tetraethylammonium bromide, tetramethyl-
35 ammonium hydroxide, tetrabutylammonium chloride, tetrabutylammonium
bromide, tetrabutylammonium hydroxide, trimethylbenzylammonium chloride,
trimethylbenzylammonium bromide, methyltricaprylryl halide,

methyltricaprylryl hydroxide, and trimethylbenzylammonium hydroxide. Preferred are methyltricaprylryl halide or hydroxide.

In another embodiment, the invention is a method for producing a polyfluorinated polyether comprising the step of reacting a fluorinated epoxide having the structure given supra with a basic compound in solvent or neat to produce the polyfluorinated polyether as given supra. Suitable bases for use in this reaction include, but are not limited to, trialkylamines of formula $R_1R_2R_3N$, where R_1 - R_3 are independently C_1 - C_6 alkyl; pyridine, sodium or potassium alkoxides (e.g., methoxide, ethoxide, t-butoxide), and sodium or potassium hydroxide.

The polyfluorinated epoxides of this invention having the structure:



can be reacted with a variety of compounds (as illustrated in Examples 3-6, 8) to afford new compounds comprised of the structure:



20

GLOSSARY

Term "F-" in a compound name designates that the compound is perfluorinated.

EXAMPLES

EXAMPLE 1

Preparation of 1,1-Bis(trifluoromethyl)ethylene Oxide (1)

Hexafluoroisobutene $\text{CH}_2=\text{C}(\text{CF}_3)_2$ (25 ml, 40 g) was condensed in a flask containing a solution of NaOCl (made at -5 to -3°C by bubbling 15 g of chlorine into mixture of 50 ml of 50 wt. % of NaOH and 100 ml of water) and 0.5 g of phase transfer catalyst - methyltricaprylammonium chloride (AliquatTM-336, Aldrich) was added at -2 to $+2^\circ\text{C}$ under vigorous stirring. Reaction mixture was agitated at this temperature for 1-1.5 hours.

The resulting reaction product was transferred out of the reactor in vacuum, collected in a cold trap (at -78°C) and distilled to give 37.5 g (yield 86%) of liquid, b.p. 41 - $42^\circ\text{C}/760$ mm Hg, which was identified as 1,1-bis(trifluoromethyl)ethylene oxide (1). The resulting compound 1 was established to have the indicated structure based upon the analytical data obtained as indicated below.

^1H NMR: 3.28 (s) ppm

^{19}F NMR: -73.34 (s) ppm

^{13}C {H} NMR: 46.75 (s), 54.99 (sept, 37 Hz), 126.76 (q, 275 Hz)

IR (gas, major): 1404 (s), 1388 (s), 1220 (s), 1083 (s), 997 (m), 871 (m),

5 758 (w), 690 (m), 636 (w) cm^{-1}

Anal. Calcd for $\text{C}_4\text{H}_2\text{F}_6\text{O}$: C, 26.68, H1.12. Found: C, 27.64, H, 1.10

EXAMPLE 2

Synthesis of $\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{OCH}_2\text{C}(\text{CF}_3)_2\text{OH}$

(2)

10 A dry 5-L round bottom flask equipped with mechanical stirrer, condenser and addition funnel was flushed with nitrogen and charged with 14.2 g (0.59 mol) of 95% sodium hydride and 400 mL of anhydrous DMF. This mixture was cooled to 10°C and 41.6 g (1.85 g, 0.47 mol) of 2-hydroxyethylvinyl ether was added dropwise over 1/2 hr. An additional 250 mL of DMF were added and the mixture
15 was stirred for 1 hr. 1,1-Bis(trifluoromethyl)ethylene oxide (1, Hexafluoro-isobutylene epoxide) (85 g, 0.47 mol) was added over 1 hr at 20-23°C. The resulting suspension was stirred for 22 hr. It was then transferred to a one-neck flask and most of the DMF was removed on a rotary evaporator at 0.1 mm and 29°C. The residue was dissolved in 250 mL of water and 10% hydrochloric acid
20 was carefully added until the solution pH was about 8. An oil which separated was collected, washed with water and dried over a mixture of anhydrous sodium sulfate and potassium carbonate. The mixture was filtered and the filtrate was distilled in a Kugelrohr apparatus at 0.5 mm and 50-59°C from a small amount of anhydrous potassium carbonate to give 89 g (71%) of oil which was stored over
25 potassium carbonate and characterized to be compound 2. ^1H NMR (δ , C_6D_6) 3.12 (d, 2H), 3.28 (d, 2H), 3.60 (s, 2H), 3.90 (d, 1H), 4.07 (d, 1H), 6.20 (dd, 1H). ^{19}F NMR (δ , C_6D_6) -76.89 (s).

EXAMPLE 3

Reaction of 1 with $(\text{CH}_3)_3\text{COK}$

30 18 g of 1 was added dropwise to a solution of 12 g $(\text{CH}_3)_3\text{COK}$ in 100 ml of dry dimethylformamide over period of 1 h to keep temperature of reaction mixture at 5 to 10°C. After addition was finished the reaction mixture was allowed to warm up to 25°C and kept at this temperature for 1 h. The reaction mixture was poured into a 200 ml of cold solution of 10% hydrochloric acid,
35 extracted with CH_2Cl_2 (2 x 50 ml), dried over MgSO_4 , solvent was removed and the residue was distilled to give 13.5 of liquid b.p. 139-140°C, which is the product $(\text{CH}_3)_3\text{COCH}_2\text{C}(\text{CF}_3)_2\text{OH}$, 95% purity.

^1H NMR: 1.26 (3H, s), 3.80 (2H, s), 4.20 (1H, br s) ppm

^{19}F NMR: -76.24 (s) ppm

EXAMPLE 4

Reaction of 1 with $\text{C}_6\text{H}_5\text{NH}_2$

15 g of 1 was added dropwise to 10 ml of $\text{C}_6\text{H}_5\text{NH}_2$ with stirring over
5 period of 1 h to keep temperature of reaction mixture below 25°C . After addition
was finished the reaction mixture was allowed to warm up to 25°C , kept at this
temperature for 16 h and distilled to give 15 g of material b.p. $112\text{--}113^\circ\text{C}/10\text{ mm}$
Hg, which crystallized upon standing, m.p. $34\text{--}35^\circ\text{C}$. The product has a structure
 $\text{C}_6\text{H}_5\text{NHCH}_2\text{C}(\text{CF}_3)_2\text{OH}$.

10 ^1H NMR: 3.75 (2H, s), 4.30 (1H, br s), 4.20 (1H, br s), 6.80 (2H, d), 6.95
(1H, t), 7.32 (2H, t) ppm

^{19}F NMR: -77.92 (s) ppm

Anal. Calcd for $\text{C}_{10}\text{H}_9\text{F}_6\text{NO}$: C, 43.97, H, 3.32, F, 41.73, N, 5.13. Found:
C, 43.46, H, 3.26, F, 40.53, N, 5.09.

15 EXAMPLE 5

Reaction of 1 with 4-F- $\text{C}_6\text{H}_4\text{NH}_2$

10 g of 1 was added dropwise to a solution of 5 g of 4-F- $\text{C}_6\text{H}_4\text{NH}_2$ in
10 ml of CH_2Cl_2 with stirring. After addition finished the reaction mixture was
allowed to warm up to 25°C , kept at this temperature for 16 h, solvent was
20 removed, the residue was distilled to give 12 g of material b.p.
 $116.5\text{--}118.5^\circ\text{C}/12\text{ mm}$ Hg, which crystallized upon standing, m.p. $34\text{--}36^\circ\text{C}$. The
product has a structure 4-F- $\text{C}_6\text{H}_4\text{NHCH}_2\text{C}(\text{CF}_3)_2\text{OH}$.

^1H NMR: 3.64 (2H, s), 4.20 (2H, br s), 6.80 (2H, d), 6.75 (2H, m), 6.93
(2H, t) ppm

25 ^{19}F NMR: -77.94 (6F, s), -123.08 (1F, m) ppm

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{F}_7\text{NO}$: C, 41.25, H, 2.77, F, 45.67, N, 4.81. Found:
C, 41.00, H, 2.70, F, 45.78, N, 4.73.

EXAMPLE 6

Reaction of 1 with $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{SH}$

30 4.5 g of 1 was added dropwise with stirring to a solution of 9.5 g of
 $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{SH}$ in 50 ml of dry dimethylformamide, to keep temperature below
 25°C . After addition finished the reaction mixture was kept at 25°C for 16 h,
poured into 100 ml of cold solution of 10% solution of HCl, the organic layer was
separated, dried over P_2O_5 and distilled to give 6 g of material b.p.
35 $25\text{--}26^\circ\text{C}/0.1\text{ mm}$ Hg. The product has a structure
 $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{SCH}_2\text{C}(\text{CF}_3)_2\text{OH}$.

^1H NMR: 2.50 (2H, m), 2.88 (2H, m), 3.18 (2H, s), 4.15 (1H, br s), ppm

^{19}F NMR: -77.90 (6F, s), -81.39 (3F, tt), -114.60 (2F, m), -122.36 (2F, m), -123.34 (2F, m), -123.83 (2F, m), -126.64 (2F, m) ppm

EXAMPLE 7

Reaction of 1 with C_6H_6

5 10 g of 1 was added dropwise at 10°C to a mixture of 20 g of C_6H_6 and 0.5 g of anhydrous AlCl_3 , stirred at 10°C for 1 h and poured on ice. Organic layer was separated, dried over MgSO_4 and distilled to give 9 g of material b.p. 101-103/53 mm Hg, which was found to be $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{CF}_3)_2\text{OH}$.

^1H NMR: 2.75 (1H, br s), 3.31 (2H, s), 7.28 (2H, m), 7.42 (3H, m) ppm

10 ^{19}F NMR: -75.39 (s) ppm

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{F}_6\text{O}$: C, 45.53, H, 3.12, F, 44.15. Found: C, 46.30, H, 3.32, F, 43.94.

EXAMPLE 8

Reaction of 1 with HOSO_2CF_3

15 4 g of 1 was added dropwise at 10°C to 10 ml of HOSO_2CF_3 to keep temperature below 30°C . The reaction mixture was stirred at 25°C for 3 h and poured on ice. Organic layer was separated, dried over MgSO_4 and distilled to give 8 g of material, which was found to be $\text{CF}_3\text{SO}_2\text{OCH}_2\text{C}(\text{CF}_3)_2\text{OH}$.

^1H NMR: 4.53 (2H, br s), 3.31 (1H, br s) ppm.

20 ^{19}F NMR: -74.74 (3F, s), -76.24 (6F, s) ppm

IR (major): 3507 (m), 1426 (s), 1226 (s), 1146 (s), 982 (s), 823 (w) cm^{-1} .

EXAMPLE 9

Preparation of 1-Methoxy-*F*-2,2-Dimethylethylene Oxide

Olefin $\text{CH}_3\text{OCF}=\text{C}(\text{CF}_3)_2$ (4.8 g) was added dropwise into a flask
25 containing a solution of NaOCl (made at -5 to -3°C by addition of 2.5 ml of chlorine into solution of 10 ml 50% NaOH in 20 ml of water) and 0.3 g of phase transfer catalyst - methyl tricaprylyl ammonium chloride (AliquatTM-336, Aldrich) at -2 to 0°C under vigorous stirring. Reaction mixture was kept at this temperature for 40 min, diluted with water, organic layer (lower) was separated,
30 washed with water, dried over MgSO_4 and analyzed. Based on NMR data crude product was found to be a mixture of 80% of 1-methoxy-*F*-2,2-dimethylethylene oxide and 20% of $(\text{CF}_3)_2\text{CClC}(\text{O})\text{OCH}_3$.

Epoxide: ^1H NMR : 3.53 (d, 1 Hz) ppm.

35 ^{19}F NMR: -69.06 (3F, dt, 8; 19 HZ), -64.40 (3F, qd, 8; 1 Hz), -110.90 (1F, m) ppm.

IR: 1490 (s, epoxide), cm^{-1} .

COMPARATIVE EXAMPLE 1Attempt of Oxidation of $C_4F_9CH=CH_2$

- In an attempted reaction of 5 g of $C_4F_9CH=CH_2$ with solution of NaOCl (made out of 10 ml of 50% NaOH, 20 ml of H_2O , 3 ml of chlorine) and 0.3 g of phase transfer catalyst - methyl tricaprylyl ammonium chloride (Aliquat™-336, Aldrich) at -2 to 0°C for 2 h only starting fluoroolefin was recovered and no detectable reaction products were found.

EXAMPLE 10Preparation of *F*-1-Methyl-1-n-Propylethylene Oxide

- Olefin $CF_2=C(OC_3F_7-n)CF_3$ (60 g) was added dropwise into a flask containing a solution of NaOBr (made at -5 to -3°C by addition of 12 ml of bromine into solution of 20 g NaOH in 150 ml of water) and 100 ml of CH_3CN at -2 to 0°C under vigorous stirring. Reaction mixture was kept at this temperature for 4 hours, diluted with water, organic layer (lower) was separated, washed with water, dried over P_2O_5 and distilled to give 54 g (yield 86%) of liquid, b.p. 56-57°C, identified as *F*-1-methyl-1-n-propoxyethylene oxide.

^{19}F NMR: -79.57 (3F, s), -85.81 (3F, t), -87.29 (2Fm), -114.59 (2F, m), -134.00 (2F, m) ppm.

IR: 1517 (s), epoxide, cm^{-1} .

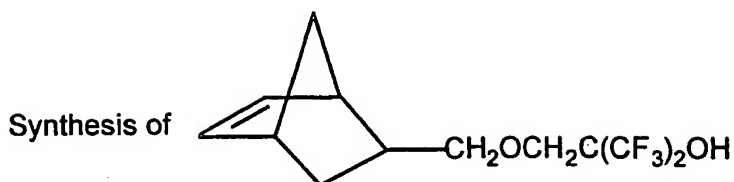
- EXAMPLE 11

Polymerization of 1,1-Bis(trifluoromethyl)ethylene Oxide

- To 5 g of epoxide (1) in a glass reactor 2 drops of dry triethylamine were added and glass reactor was left at 25°C. After 12 hours no liquid, but only white solid was found inside of reactor. The material was not soluble in solvents such as tetrahydrofuran or diglyme, CFC-113, but it was slightly soluble in acetone and fairly soluble in C_6F_6 . Data of 1H , ^{19}F and ^{13}C NMR of polymer solution in C_6F_6 are consistent with the structure of polyether (i.e., ring opened polymer having the structure shown below:

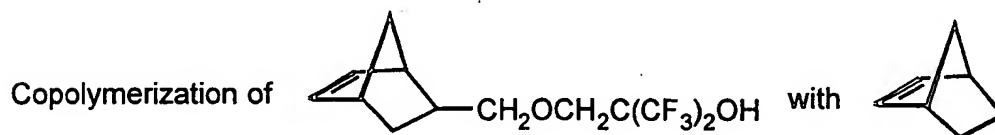
- $(-C(CF_3)_2-CH_2-O-)_n$

Molecular weight calculated based on NMR data was in the range 3000-5000. Based on DSC, this polymer has a sharp melting point at 148.8°C (second heat) and started to decompose at temperature over 350°C.

EXAMPLE 12

5 Hexafluoroisopropanol-substituted norbornene

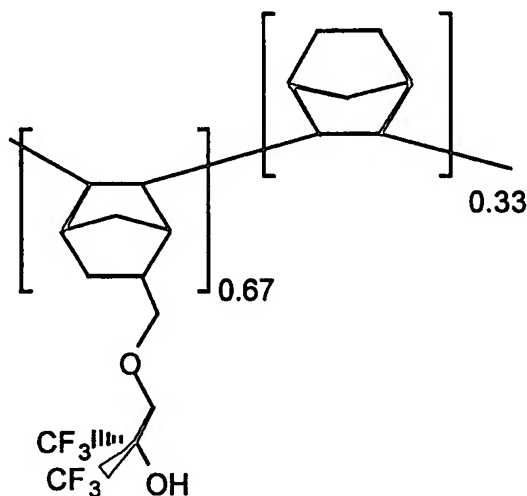
A dry round bottom flask with mechanical stirrer and condenser was charged under nitrogen with 28.8 g (1.2 mol) of 95% sodium hydride and 400 mL of anhydrous DMF. 5-Norbornene-2-methanol (108.6 g, 0.875 mol) was added dropwise at room temperature over 0.5 hr. The resulting mixture was stirred for 3 hr. 1,1-Bis(trifluoromethyl)ethylene oxide (1, Hexafluoroisobutylene epoxide) (173.2 g, 0.96 mol) was added dropwise over 2 hr. The resulting mixture was stirred for 72 hr at room temperature. DMF was evaporated on a rotary evaporator at 45°C and 1 mm. The residue was diluted with 300 mL of ice water containing 30 mL of glacial acetic acid. A lower layer was separated and the aqueous layer was extracted with 2 X 25 mL of methylene chloride. The combined organic layers were washed with 3 X 100 mL of water, dried over anhydrous magnesium chloride, filtered and distilled under vacuum in a Kugelrohr apparatus at 65-87°C and 0.1 mm. An NMR spectrum revealed that the product was contaminated with small amounts of DMF so it was dissolved in 100 mL of hexane, washed with 4 X 200 mL water, dried over anhydrous magnesium sulfate, filtered and distilled in a Kugelrohr apparatus at 70-80°C and 0.1 mm giving 233.9 g (88%) of the title product (hexafluoroisopropanol-substituted norbornene, compound 3). In another preparation, the product was distilled through a 12" Vigreux column indicating a bp of 52-53°C at 0.1 mm. ¹H NMR (δ, CD₂Cl₂) 0.5 to 4.3 (complex multiplets, 12 H), 5.90, 6.19 and 6.26 (m, 2H). ¹⁹F NMR (δ, CD₂Cl₂) -77.4 (s).

EXAMPLE 13

by vinyl-addition polymerization

Under nitrogen, 0.125 g (0.319 mmol) of allyl palladium complex $[(\eta^3\text{-MeCHCHCH}_2)\text{PdCl}]_2$ and 0.219 g (0.637 mmol) silver hexafluoro-

antimonate were suspended in chlorobenzene (40 mL). The resulting mixture was stirred at room temperature for 15 minutes. It was then filtered to removed precipitated AgCl. To the resulting gold-colored solution was added a solution of 6.46 g (21.2 mol) of the hexafluoroisopropanol-substituted norbornene and 1.00 g norbornene (10.62 mmol) dissolved in 5 mL chlorobenzene. The resulting reaction mixture was stirred overnight at room temperature. The reaction mixture was then concentrated to dryness and the polymer washed with hexane and dried in a vacuum oven. Yield = 7.48 g of addition polymer. ¹H NMR (CD₂Cl₂) of the polymer was consistent with a random copolymer structure with the approximate molar composition shown below:



EXAMPLE 14

Synthesis of 1,1-Bis(trifluoromethyl)-2-Chloromethyl Oxirane

Using 100 ml of NaOCl (Aldrich, 12% chlorine available), 0.5 g of phase transfer catalyst, tricaprylmethylammonium chloride (Aliquat™-336, Aldrich) and 28 g of (CF₃)₂C=CHCH₂Cl, which is added slowly at 5-15°C, after stirring reaction mixture for 1h at 15-20°C and separation of layer, there is isolated 26 g of crude product, containing 84% epoxide and 16% of (CF₃)₂CHCH=CHCl (NMR). Distillation of crude material using short spinning-band column give 7 g (78% calculated and 25% isolated yield respectively) of epoxide 98% purity, b.p. 88.2-88.6°C. NMR: ¹H (acetone-d₆): 4.12 (1H, m), 3.95 (1Hm), 4.20(1H,m); ¹⁹F: 74.11 (3F, q; 7Hz), -67.21(3F, q;7Hz); ¹³C (proton decoupled) 34.42(q; 4Hz), 58.94(q; 3Hz), 59.53(sept.; 40Hz), 120.37(q. ; 281Hz), 120.96(q.; 281Hz). IR : 1459 cm⁻¹.

EXAMPLE 15Synthesis of 1,1-Bis(Perfluoroethyl)-2-*n*-Perfluoropropyl Oxirane

Using 18 ml of NaOCl (Aldrich, 12% chlorine available), 0.2 g of phase transfer catalyst (Aliquat™-336, Aldrich, tricaprylylmethylamonium chloride) and 3 g of (C₂F₅)₂C=CHC₃F₇, which is added slowly at 5-15°C, after stirring reaction mixture at 15-20°C for 15 h, separation of lower layer it is isolated 2.5 g of crude product, which is based on NMR data epoxide of >98% purity. Yield is 83%. IR: 1354; 1353 cm⁻¹; ¹H NMR

(CDCl₃): 3.85 (d,d); ¹⁹F NMR: -81.55 (3F, d), -80.92(3F, t), -81.10 (3F, t), -11.50 (2F, AB pattern), -119.00 (2F, AB pattern), -119.80 (2F, AB pattern), -127.80 (2F, AB pattern).

EXAMPLE 16Synthesis of CH₂(O)C[C(CF₃)₂OH]C(O)OCH₃ (3)

Using 30 ml of NaOCl (Aldrich, 12% chlorine available), 0.2 g of phase transfer catalyst (Aliquat-336, Aldrich, tricaprylylmethylamonium chloride) and 7 g of CH₂=C[C(CF₃)₂OH]C(O)OCH₃, which is added slowly at 5-15°C, after stirring reaction mixture at 15-20°C for 1.5 h, reaction mixture is filtered. There is isolated 4.0 g of product which, based on NMR data, is epoxide 3 of >98% purity, m.p. 56-58°C. Yield is 57%. IR: 1744; 1450 cm⁻¹; ¹H NMR (CDCl₃): 3.15 (1H, d, 5.6Hz) 3.25 (1H, d, 5.6Hz); 3.87 (3H, s), 4.7 (1H, br.s); ¹⁹F NMR: -66.39 (3F, q, 7.2Hz), -73.28(3F, q, 7.2Hz).

EXAMPLE 17Synthesis of CH₂(O)C[C(CF₃)₂OH]C(O)OCH₃ (4)

Using 18 ml of NaOCl (Aldrich, 12% chlorine available), 0.2 g of phase transfer catalyst (Aliquat-336, Aldrich, tricaprylylmethylamonium chloride) and 4 g of CH₂=C[C(CF₃)₂OH]C(O)OCH₃, which is added slowly at 5-15°C, after stirring reaction mixture at 15-20°C for 1.5 h, reaction mixture is filtered and there is isolated 2.5 g of product which, based on NMR data, is epoxide 4 of >98% purity, m.p. 148-150°C. Yield is 83%.

What is claimed is:

1. A method for producing a fluorinated epoxide comprising the step of reacting a fluorinated ethylenically unsaturated compound having the structure:

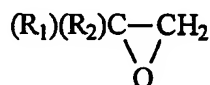


with a metal hypohalite oxidizing agent in the presence of a phase transfer catalyst to produce the fluorinated epoxide having the structure:

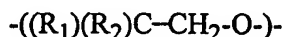


wherein R_1 is selected from the group consisting of H and OR, where R is C_1 - C_{10} alkyl; R_2 is selected from the group consisting of H and F; R_3 and R_4 are selected from the group consisting of C_1 - C_{10} perfluoroalkyl and C_1 - C_{10} perfluoroalkoxy.

15 2. A method for producing a polyfluorinated polyether comprising the step of reacting a fluorinated epoxide having the structure:



20 with a basic compound in solution to produce the polyfluorinated polyether having the repeat unit:



25 wherein R_1 and R_2 are independently C_1 - C_{10} perfluoroalkyl.

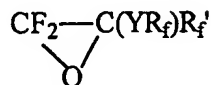
3. A fluorine-containing polymer comprising a repeat unit derived from at least one ethylenically unsaturated compound containing a fluoroalcohol functional group having the structure:



wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms or taken together are $(CF_2)_n$ wherein n is 2 to 10; and X is selected from the group consisting of sulfur, oxygen, nitrogen, phosphorous, other Group Va element, and other Group VIa element.

4. The polymer of Claim 3 wherein R_f and R_f' are CF_3 and X is oxygen.

5. A perfluorinated epoxide having the structure:



5 where R_f and R_f' are the same or different perfluoroalkyl groups of from 1 to 10 carbon atoms or taken together are $(\text{CF}_2)_n$ wherein n is 2 to 10; and Y is selected from the group consisting of sulfur and oxygen.

6. The perfluorinated 2-alkoxypropene epoxide of Claim 5 wherein Y is oxygen, R_f is selected from the group consisting of trifluoromethyl, pentafluoroethyl and heptafluoropropyl, and R_f' is trifluoromethyl.

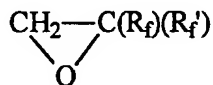
7. A method for incorporating a fluoroalcohol functional group having the structure:



15 into a polymer as a pendant group, wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms or taken together are $(\text{CF}_2)_n$ wherein n is 2 to 10; and X is selected from the group consisting of sulfur, oxygen, nitrogen, phosphorous, other Group Va element, and other Group VIa element;

said method comprising the steps of:

a. reacting an epoxide having the structure:



25 with an ethylenically unsaturated compound containing substituent X to produce an ethylenically unsaturated comonomer comprised of the structure:

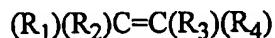


and

b. polymerizing a reaction mixture comprised of the ethylenically unsaturated comonomer to produce the polymer.

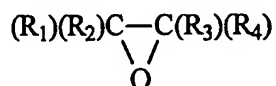
8. The method of Claim 7 where X is oxygen and R_f and R_f' are CF_3 .

9. A method for producing a fluorinated epoxide comprising the step of reacting a fluorinated ethylenically unsaturated compound having the structure:



5

with a metal hypohalite oxidizing agent in the presence of a phase transfer catalyst to produce the fluorinated epoxide having the structure:



10

wherein R_1 is selected from the group consisting of H and OR, where R is C_1 - C_{10} alkyl; R_2 is selected from the group consisting of H, F, C_1 - C_{10} perfluoroalkyl, and X-substituted C_1 - C_{10} alkyl, wherein X is F, Cl, Br, I, OH, or OR; R_3 and R_4 are each independently selected from the group consisting of C_1 - C_{10} perfluoroalkyl, $C(R_f)(R_f')OH$, C_1 - C_{10} perfluoroalkoxy, C_1 - C_{10} carboalkoxy, and hydroxy-substituted C_1 - C_{10} carboalkoxymethyl-substituted C_1 - C_4 perfluoroalkyl.

15

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60/132,453 4 May 1999 (04.05.1999) US
- (71) Applicant (*for all designated States except US*): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): PETROV, Viacheslav, Alexandrovich [US/US]; 2 Cappa Court, Hockessin, DE 19707 (US). FEIRING, Andrew, Edward [US/US]; 7 Buckridge Drive, Wilmington, DE 19807 (US). FELDMAN, Jerald [US/US]; Brackenville Woods, 16 Cinnamon Drive, Hockessin, DE 19707 (US).
- (74) Agent: MAGEE, Thomas, H.; E.I. Du Pont De Nemours And Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).
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— With international search report.
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- (88) Date of publication of the international search report:
22 March 2001
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: POLYFLUORINATED EPOXIDES AND ASSOCIATED POLYMERS AND PROCESSES

(57) Abstract: A method for producing partially fluorinated epoxides and corresponding polyether homopolymers of these polyfluorinated epoxides is described. Also described is a method for incorporating a fluoroalcohol functional group into a polymer as a pendant group. Certain perfluorinated olefins are also described. These polyfluorinated epoxides and the associated polymers and methods relating to them are useful components in photoresists, particularly in lithographic photoresists for use at low ultraviolet wavelengths (e.g., 157 nm).



WO 00/66575 A3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/11746

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D303/48 C07D303/08 C07D301/26 C07D301/03 C08G65/00
C08F16/26 C08G65/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D C08G C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, BEILSTEIN Data, EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 573 330 A (ROBERT E. A. DEAR) 30 March 1971 (1971-03-30)	1,9
A	example 2	5,6
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A	page 2294, right-hand column, last paragraph	5,6
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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Z document member of the same patent family

Date of the actual completion of the international search

29 November 2000

Date of mailing of the international search report

09. 01. 2001

Name and mailing address of the ISA

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O'Sullivan, T

INTERNATIONAL SEARCH REPORT

Intor. nal Application No

PCT/US 00/11746

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Intor. onal Application No

PCT/US 00/11746

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 084 583 A (ROZEN SHLOMO M ET AL) 28 January 1992 (1992-01-28) claim 1 example 4 ---	2
P,X	WO 00 17712 A (FEIRING ANDREW EDWARD ;DU PONT (US); FELDMAN JERALD (US)) 30 March 2000 (2000-03-30) example 42 ---	3,4,7,8
A	EP 0 889 028 A (DU PONT) 7 January 1999 (1999-01-07) example 126 ---	3,4,7,8
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/11746

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1,9

A process for preparing fluorinated epoxides of formula

$$(R1)(R2)C \begin{smallmatrix} \text{---} \\ \text{O} \end{smallmatrix} C(R3)(R4)$$

2. Claim : 2

A process for preparing polyfluorinated polyethers using as starting materials certain epoxides prepared in claims 1 or 9.

3. Claims: 3,4,7,8

Polymers containing a fluoroalcohol functional group prepared by using as starting materials some epoxides prepared in claims 1 and 9

4. Claims: 5,6

Certain perfluorinated epoxides of formula:

$$CF_2 \begin{smallmatrix} \text{---} \\ \text{O} \end{smallmatrix} C(YRf)Rf'$$

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Appl. No.

PCT/US 00/11746

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/11746

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